

CHEMICAL STUDIES OF THE AMES OXYDESULFURIZATION PROCESS

Thomas G. Squires, Clifford G. Venier, Lawrence W. Chang, and Thomas E. Schmidt

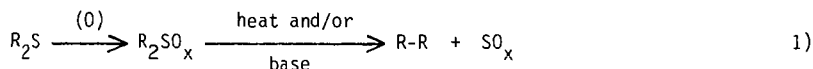
Ames Laboratory*, Iowa State University, Ames, Iowa 50011

In freshly mined coal, sulfur is present in two major forms: as iron pyrite and as organic sulfur, i.e., as sulfur chemically bonded to carbon and thus comprising an integral part of the organic coal matrix(1). The pyritic sulfur is distributed in varying proportions between large framboidal pyrite, the major portion, and microfine pyrite which is encapsulated in the organic coal matrix. While the majority of the pyrite can usually be removed by conventional physical beneficiation processes, encapsulated microfine pyrite as well as organic sulfur are not responsive to these cleaning procedures. Consequently, a number of chemical oxydesulfurization procedures have been proposed and investigated in order to supplement the physical beneficiation of coal. One of these techniques, the Ames Process(2), utilizes 0.2 M aqueous Na_2CO_3 at 150°C under a pressure of 200 psi O_2 for one hour.

Some of the early model compound work on the Ames Process was done by Greer and Wheelock(3). These workers investigated the effect of the Ames Process on iron pyrite and were able to demonstrate quite dramatically that pyrite (FeS_2) is converted to hematite (Fe_2O_3) under the process conditions.

The assessment of the efficacy of the Ames Process in removing organic sulfur from coal is much more complicated due to the inaccuracy of the ASTM method for determining organic sulfur in coal and the paucity of information detailing the organic sulfur functional group distribution in coal. The inaccuracy of the quantitative method for determining organic sulfur can be attributed partially to a lack of precision in the ASTM method of determining organic sulfur by difference, which Paris(4) has found to be as high as $\pm 25\%$ at two standard deviations. An additional source of error has been shown by Greer(5) to involve organically encapsulated microfine pyrite. While this pyrite would be inert to extraction with nitric acid in the raw coal and thus would report as organic sulfur, subjecting the coal to $150\text{--}200^\circ\text{C}$ for an hour in the presence of water and oxygen should remove this microfine pyrite or, at least, render it accessible to the nitric acid extraction. The data generated from the treated coal would indicate an apparent removal of organic sulfur. On the basis of these considerations, the evaluation of organic sulfur removal by the ASTM method could easily be in error by as much as $\pm 50\%$ of the raw coal value. Since both the PETC and Ames Oxydesulfurization Processes claim the removal of organic sulfur from coal up to a maximum of 40%, we set out to assess the validity of these claims by subjecting model compounds to the Ames conditions.

Conceptually, this type of oxydesulfurization has been described as a two step process involving initial oxidation at sulfur to produce sulfoxides and sulfones. This step is then though to be followed by the thermal and, in the Ames Process,



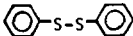



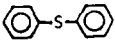
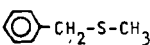


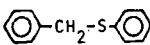





base assisted extrusion of SO_x . In this formulation, the initial oxidation at sulfur facilitates desulfurization by polarizing and weakening the carbon to sulfur bond(6).

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The results for model compounds are presented in Table 1. The lack of reactivity exhibited was surprising. In order to assess the possibility that coal may act as a catalyst in the oxidation, reactions of several compounds were carried out in the presence of coal. These results are shown in Table 2.

TABLE 1. EFFECT OF AMES PROCESS ON MODEL ORGANIC SULFUR COMPOUNDS^a

MODEL COMPOUND	RECOVERED STARTING MATERIAL	YIELDS	
		PRODUCTS	
	0%	 (95%)	
	5%	 (90%)	
	96%	No reaction	
	87%	No reaction	
	98%	No reaction	
(n-C ₈ H ₁₇) ₂ S	90%	No reaction	
	36%	 (23%),  (34%), CH ₃ SO ₃ Na (55%)	
	29%	 (31%),  (18%),  (51%)	

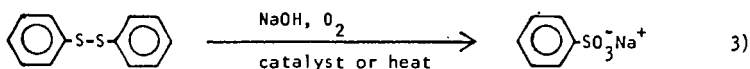
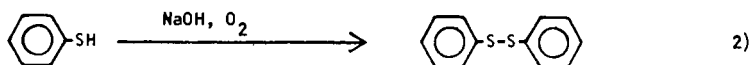
^a150°C, 200 psi O₂, 0.2M aqueous Na₂CO₃, 1 hour.

TABLE 2. EVALUATION OF POSSIBLE COAL CATALYSIS IN AMES PROCESS

Model Compound	Yield of Recovered Starting Material		
	Model Compound Alone	Lovilia Coal Added	
		N ₂	O ₂
Dibenzothiophene	96%	83%	76%
Diphenyl Sulfide	98	76	74
Diocetyl Sulfide	90	--	82
Benzyl Methyl Sulfide	36	75	13


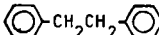
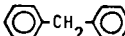
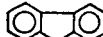
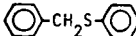
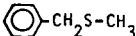
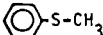
In order to take into account the decreased recovery expected due to adsorption of the model compounds onto coal, runs using both oxygen and nitrogen were performed. The results confirm that simple sulfides and dibenzothiophene, the principle functional groups expected to be in coal, are inert to oxidation under the Ames Process conditions.

Of the reactive functions, thiophenols are widely known to undergo facile air oxidation to disulfides (7) and the oxidation of thiophenols and disulfides to sulfonic acids under more forcing conditions is also known (8). That leaves the results of the reaction of two compounds, benzyl methyl sulfide and benzyl phenyl



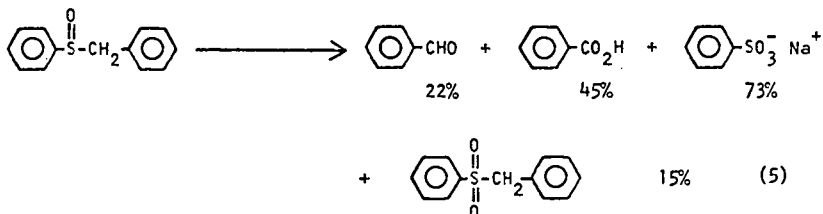
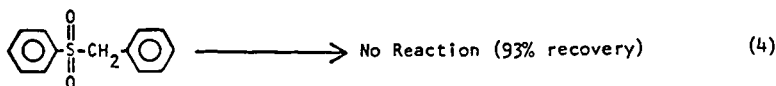
sulfide, to be explained. The fact that it is only the benzylic sulfides which are reactive is reminiscent of hydrocarbon autoxidation, a long known and well studied process which involves the free radical abstraction of hydrogen from weak carbon-hydrogen bonds (9). Table 3 presents the relative rates of hydrogen abstraction from some representative compounds by phenyl radical (10), the most studied of the hydrogen abstractors and t-butylperoxy radical (11), more closely similar to the peroxy radicals which we postulate would be the hydrogen abstracting species in the Ames Process, as well as the autoxidation rate of the pure compounds.

TABLE 3. RELATIVE RATES OF HYDROGEN ABSTRACTION BY FREE RADICALS

Compound	Ph \cdot , 60°C ^a	(CH ₃) ₃ COO \cdot , 30°C ^b	RH + ROO \cdot , 30°C ^b
	(1.0)	(1.0)	(1.0)
	3.6	5.0	2.3
	5.1	8.9	8.3
	13.	---	---
	17.	4.4	40.
	8.2	---	---
	1.4	---	---

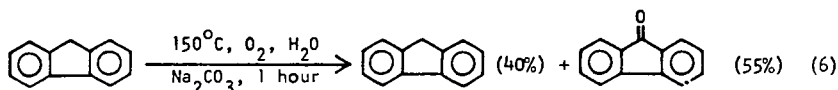
^aData of reference 10. ^bData of reference 11.

In order to rule out the possibility that the benzylic sulfides are in fact oxidized to either the sulfoxide or sulfone, which then are responsible for the observed products, both benzyl phenyl sulfoxide and benzyl phenyl sulfone were subjected to the reaction conditions. Because the sulfone is inert, it can be ruled out as a possible reaction intermediate. Although it does react, the sulfoxide gives sulfone as one of the products. Since sulfone is not isolated in the oxidation of sulfide under process conditions, the sulfoxide is also eliminated as a



possible reaction intermediate.

Beside benzylic sulfides, one would expect that some hydrocarbons, for example, fluorene, would also be reactive to the oxydesulfurization conditions. Under Ames process conditions, fluorene is indeed degraded to its known autoxidation product, fluorenone(13). While we have not yet run other hydrocarbons which might be expected to be reactive, we believe that they will behave similarly.



Fledgling studies of sulfur-containing synthetic polymers(14) add support to the model compound studies. Table 4 shows the results of subjecting three modified polystyrenes to the Ames Process conditions. Both the phenylthiomethyl and tolylthiomethyl polystyrenes are analogs of the model compound, benzyl phenyl sulfide. As we had anticipated, the solid polymers, which should be better models for solid coal, were reactive, but less so than the corresponding model compound. Polystyrene cross-linked by dibenzothiophene is unreactive, confirming the inertness of the dibenzothiophene moiety to oxydesulfurization.

TABLE 4. EFFECT OF THE AMES PROCESS ON SULFUR-CONTAINING POLYSTYRENE POLYMERS^a

Polymer ^b	%Sulfur Removed
$\text{P}-\text{CH}_2-\text{S}-\text{C}_6\text{H}_5$	10%
$\text{P}-\text{CH}_2-\text{S}-\text{C}_6\text{H}_4-\text{CH}_3$	20%
$\text{P}-\text{CH}_2-\text{DBT}-\text{CH}_2-\text{P}$	0

^a150°C, 200 psi O₂, 0.2 M aqueous Na₂CO₃, 1 hour.

^b(P) = polystyrene backbone; substituents are attached through the para position.

DBT = dibenzothiophene nucleus,

Finally, we have subjected the pyridine extract of an Illinois #6 coal to the Ames Process conditions. All of the sulfur in an extract is organically bound and hence, the quite accurate total sulfur determination is also the organic sulfur determination. The results in Table 5 show that oxydesulfurization apparently does not reduce the organic sulfur level of the extract. On the other hand, some of the extract is apparently oxidized as judged by the increase in S/C ratio, the increase in oxygen content, and the increased O/C ratio.

Our conclusions concerning the oxydesulfurization process as gleaned from model compound studies are, in summary, the following:

1. Thiophenols and disulfides are the only groups oxidized at sulfur.
2. Sulfides, including thiophenes, are not oxidized at sulfur.
3. Reactive sulfides are oxidized at reactive carbon-hydrogen bonds.
4. Reactive carbon-hydrogen bonds in functions not containing sulfur also react.
5. The Ames Process is directly analogous to hydrocarbon autoxidation.
6. More efficient sulfur removal without severe degradation of the coal is not possible under the present process conditions.

The success which these model compound studies have had in defining the limits of the efficacy of the Ames oxydesulfurization process encourage us to believe that this approach will be quite valuable in the evaluation of other proposed chemical coal cleaning techniques.

Table 5. EFFECT OF AMES PROCESS ON PYRIDINE EXTRACT OF ILLINOIS #6 COAL^a

Datum	Extract	Ames Processed Extract	
		N ₂ ^b	O ₂ ^c
Weight recovered	--	93%	85%
Elemental Analysis ^d			
C	76.6	77.9	68.5
H	6.1	5.8	4.9
S	0.8	0.8	0.9
O (by diff.)	14.4	12.8	22.3
S/C ratio (moles)	0.028	0.026	0.034
H/C ratio (moles)	0.95	0.90	0.85
O/C ratio (moles)	0.25	0.22	0.43

^a 150°C, 0.2 M aqueous Na₂CO₃, 1 hour. ^b 200 psi N₂ pressure. ^c 200 psi O₂ pressure.



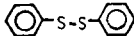

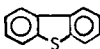

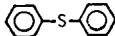
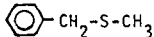


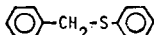



^d Samples contain a small amount of ash or NaCl. Element percents are expressed ash or NaCl free.

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14. The details of synthesis will be published in another place.

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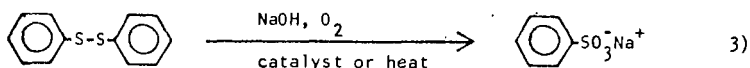
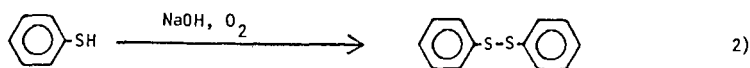
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
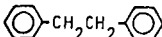
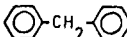

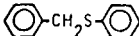
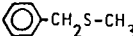
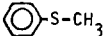
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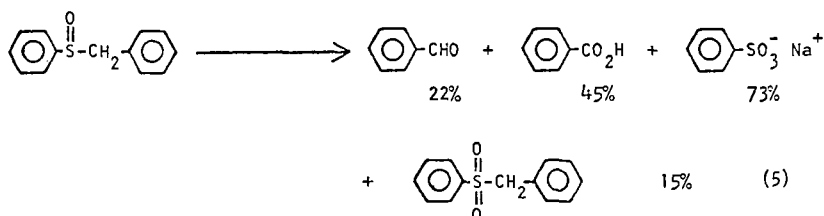
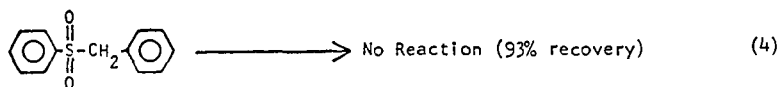
sulfide, to be explained. The fact that it is only the benzylic sulfides which are reactive is reminiscent of hydrocarbon autoxidation, a long known and well studied process which involves the free radical abstraction of hydrogen from weak carbon-hydrogen bonds (9). Table 3 presents the relative rates of hydrogen abstraction from some representative compounds by phenyl radical (10), the most studied of the hydrogen abstractors and t-butylperoxy radical (11), more closely similar to the peroxy radicals which we postulate would be the hydrogen abstracting species in the Ames Process, as well as the autoxidation rate of the pure compounds.

TABLE 3. RELATIVE RATES OF HYDROGEN ABSTRACTION BY FREE RADICALS

Compound	Ph [•] , 60°C ^a	(CH ₃) ₃ COO [•] , 30°C ^b	RH + ROO [•] , 30°C ^b
	(1.0)	(1.0)	(1.0)
	3.6	5.0	2.3
	5.1	8.9	8.3
	13.	---	---
	17.	4.4	40.
	8.2	---	---
	1.4	---	---

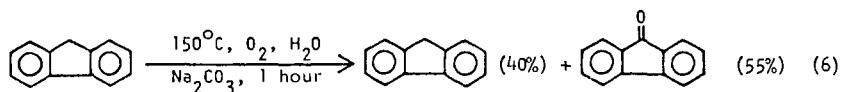
^aData of reference 10. ^bData of reference 11.

In order to rule out the possibility that the benzylic sulfides are in fact oxidized to either the sulfoxide or sulfone, which then are responsible for the observed products, both benzyl phenyl sulfoxide and benzyl phenyl sulfone were subjected to the reaction conditions. Because the sulfone is inert, it can be ruled out as a possible reaction intermediate. Although it does react, the sulfoxide gives sulfone as one of the products. Since sulfone is not isolated in the oxidation of sulfide under process conditions, the sulfoxide is also eliminated as a



possible reaction intermediate.

Beside benzylic sulfides, one would expect that some hydrocarbons, for example, fluorene, would also be reactive to the oxydesulfurization conditions. Under Ames process conditions, fluorene is indeed degraded to its known autoxidation product, fluorenone(13). While we have not yet run other hydrocarbons which might be expected to be reactive, we believe that they will behave similarly.



Fledgling studies of sulfur-containing synthetic polymers(14) add support to the model compound studies. Table 4 shows the results of subjecting three modified polystyrenes to the Ames Process conditions. Both the phenylthiomethyl and tolylthiomethyl polystyrenes are analogs of the model compound, benzyl phenyl sulfide. As we had anticipated, the solid polymers, which should be better models for solid coal, were reactive, but less so than the corresponding model compound. Polystyrene cross-linked by dibenzothiophene is unreactive, confirming the inertness of the dibenzothiophene moiety to oxydesulfurization.

TABLE 4. EFFECT OF THE AMES PROCESS ON SULFUR-CONTAINING POLYSTYRENE POLYMERS^a

Polymer ^b	%Sulfur Removed
$\text{P}-\text{CH}_2-\text{S}-\text{C}_6\text{H}_5$	10%
$\text{P}-\text{CH}_2-\text{S}-\text{C}_6\text{H}_4-\text{CH}_3$	20%
$\text{P}-\text{CH}_2-\text{DBT}-\text{CH}_2-\text{P}$	0

^a150°C, 200 psi O₂, 0.2 M aqueous Na₂CO₃, 1 hour.

^b P = polystyrene backbone; substituents are attached through the para position.

DBT = dibenzothiophene nucleus,

Finally, we have subjected the pyridine extract of an Illinois #6 coal to the Ames Process conditions. All of the sulfur in an extract is organically bound and hence, the quite accurate total sulfur determination is also the organic sulfur determination. The results in Table 5 show that oxydesulfurization apparently does not reduce the organic sulfur level of the extract. On the other hand, some of the extract is apparently oxidized as judged by the increase in S/C ratio, the increase in oxygen content, and the increased O/C ratio.

Our conclusions concerning the oxydesulfurization process as gleaned from model compound studies are, in summary, the following:

1. Thiophenols and disulfides are the only groups oxidized at sulfur.
2. Sulfides, including thiophenes, are not oxidized at sulfur.
3. Reactive sulfides are oxidized at reactive carbon-hydrogen bonds.
4. Reactive carbon-hydrogen bonds in functions not containing sulfur also react.
5. The Ames Process is directly analogous to hydrocarbon autoxidation.
6. More efficient sulfur removal without severe degradation of the coal is not possible under the present process conditions.

The success which these model compound studies have had in defining the limits of the efficacy of the Ames oxydesulfurization process encourage us to believe that this approach will be quite valuable in the evaluation of other proposed chemical coal cleaning techniques.

Table 5. EFFECT OF AMES PROCESS ON PYRIDINE EXTRACT OF ILLINOIS #6 COAL^a

Datum	Extract	Ames Processed Extract	
		N ₂ ^b	O ₂ ^c
Weight recovered	--	93%	85%
Elemental Analysis ^d			
C	76.6	77.9	68.5
H	6.1	5.8	4.9
S	0.8	0.8	0.9
O (by diff.)	14.4	12.8	22.3
S/C ratio (moles)	0.028	0.026	0.034
H/C ratio (moles)	0.95	0.90	0.85
O/C ratio (moles)	0.25	0.22	0.43

^a150°C, 0.2 M aqueous Na₂CO₃, 1 hour. ^b200 psi N₂ pressure. ^c200 psi O₂ pressure.

^dSamples contain a small amount of ash or NaCl. Element percents are expressed ash or NaCl free.